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*ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF
CONDUCTIVE POLYMER COATINGS*

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ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) was used to investigate the corrosion protection performance of twenty-nine proprietary conductive polymer coatings for cold-rolled steel under immersion in 3.55% NaCl. Corrosion potential as well as Bode plots of the data were obtained for each coating after one hour immersion in 3.55% NaCl. All coatings, with the exception of one, have a corrosion potential that is higher in the positive direction than the corrosion potential of bare steel under the same conditions. The EIS spectra of the twenty-nine coatings were characterized by an impedance that is higher than the impedance of bare steel. The twenty-nine coatings were classified into two groups based on their EIS spectra. Group A consisted of twenty-one coatings with Bode plots indicative of the capacitive behavior characteristic of barrier coatings. An equivalent circuit consisting of a capacitor in series with a resistor simulated the experimental EIS data for these coatings very well. Group B consisted of eight coatings that exhibited EIS spectra showing an inflection point which indicates that two time constants are present. This may be caused by an electrochemical process taking place which could be indicative of coating failure. These coatings have a lower impedance than those in group A.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF CONDUCTIVE POLYMER COATINGS

Luz Marina Calle

1. INTRODUCTION

Electrically conductive polymers have attracted a great deal of interest since their discovery about two decades ago. Soon after their discovery, it became clear that their unique properties could be used in several technological applications, such as the development of a new class of superconductors, light emitting plastics, polymer-based switching devices, and sensing devices. The sheer volume of fundamental and applied research in this field makes it inevitable that conductive polymers will find an increasing range of applications.¹

Polyaniline (PAN) has attracted much attention as a unique electrically conductive polymer.² Many publications revealed that this material exhibits unusual electrical and optical properties. The reversibility of these properties combined with its good environmental stability and its low cost of production makes this polymer suitable for the development of the aforementioned technological applications.³ Another possible application of PAN involves its use in protecting metals and semiconductors from corrosion.^{4,5} Investigations aimed at following the improvement of this application are justified.

In the mid 1980's, researchers at the Kennedy Space Center (KSC) in Florida became interested in PANs as protective coatings for metallic surfaces. Research has been ongoing for over 20 years at KSC to find coating materials to protect launch site structures and equipment from the extremely corrosive conditions present at the launch complexes. The combination of proximity to the Atlantic ocean and acidic combustion products from solid rocket boosters results in corrosive stresses unique to KSC.

Extensive coating testing at KSC lead to the conclusion that inorganic zinc-rich primers (ZRP) significantly outperformed organic zinc-rich type primers in the marine atmosphere of Florida. This was partially attributed to the increased conductivity of the inorganic ZRP coating film. The materials typically used to produce the organic zinc-rich films (e.g., epoxies, vinyls, etc.) produced an undesirable insulating effect on the zinc particles. This effect resulted in decreased galvanic activity of the zinc for protection of the carbon steel substrate. On the other hand, the organic zinc-rich primers had the advantage of allowing for less than perfect surface preparation on steel to achieve performance. The organic polymers provided better adhesion to marginally prepared substrates than the inorganic materials. This result led researchers at KSC to the idea of using conductive organic materials to formulate these zinc coatings in order to develop a conductive organic zinc-rich primer. The idea being that the conductive organic vehicle would provide both the increased conductivity needed for superior galvanic protection of the steel substrate and the better adhesion to less than perfectly prepared surfaces. Hence the work on

conductive organic polymers and the search for materials that would allow the production of a new generation of protective coatings based on this technology began.

The main objective of this work was to use Electrochemical Impedance Spectroscopy (EIS) to study recently developed proprietary conductive polymer coatings. These materials are either doped forms of PAN or short chain compounds based on PAN. The compounds were applied on cold-rolled steel panels as corrosion protective coatings. Corrosion potential versus time measurements were collected for an hour followed by EIS measurements. Both sets of measurements were obtained using 3.55% (w/w) sodium chloride (NaCl) solution as the electrolyte.

2. EXPERIMENTAL PROCEDURE

Test Samples

Specimens were flat cold-rolled steel type S panels (Q Panel Corporation, Cleveland) 20.2 cm (7.8 in) x 10.1 cm (4.0 in) coated on one side with a conductive polymer formulation supplied by Dr. Ed Weil from Polytechnic University in New York, NY. The panels were photographed for documentation purposes prior to any testing or exposure. Coating thickness measurements were performed using a magnetic pull-off thickness gauge and found to be in the range between 1.2 and 2.0 mils (.003 cm - .005 cm).

Corrosion Potential Measurements

Corrosion potential measurements were performed using a system manufactured by EG&G Princeton Applied Research Corporation. The system used includes: (1) the Model 273 Computer-Controlled Potentiostat/Galvanostat, (2) the Model 5210 Computer-Controlled Lock-In Amplifier, and (3) the Model 352/342 SoftCorr™ II Corrosion Measurement Software. The electrochemical cell included a Ag/AgCl (silver/silver chloride) electrode, a platinum counter electrode, the sample working electrode, and a bubbler/vent tube. The flat specimen holder in the electrochemical cell is designed such that the exposed surface area is 1 cm². Corrosion potential values were gathered for one hour in aerated 3.55% NaCl. All solutions were prepared using deionized water. Aeration with dry air was maintained throughout the test.

Electrochemical Impedance Measurements

A Model 378 Electrochemical Impedance system manufactured by EG&G Princeton Applied Research Corporation was used for all EIS measurements. The system includes: (1) the Model 273 Computer-Controlled Potentiostat/Galvanostat, (2) the Model 5210 Computer-Controlled Lock-In Amplifier, and (3) the Model M388 Electrochemical Impedance Software including circuit modeling routines. Data were gathered in the frequency range from 100 kHz to 0.01 Hz. Three experiments were performed in a sequence covering the specified frequency range, and the data were automatically merged and saved. The frequency ranges for the three experiments were

100 kHz to 5 Hz, 10 Hz to 0.1 Hz, and 0.1 Hz to 0.01 Hz. The AC amplitude used for the experiments was 10 mV. Each sample was studied after one hour immersion in aerated 3.55% NaCl.

Bode magnitude plots of the data (showing the logarithm of the modulus of the impedance, $\log |Z|$, as a function of the logarithm of frequency and phase angle, α in degrees, as a function of the logarithm of frequency) were obtained for each coating after one hour of immersion in 3.55% NaCl. The impedance data were analyzed using the Equivalent Circuit computer simulation program by B. A. Boukamp.⁶

3. RESULTS AND DISCUSSION

Table 1 shows the thickness and color of the coatings as well as the corrosion potential and the type of EIS spectra after one hour of immersion in 3.55% NaCl. All coatings, with the exception of coating 16, exhibit a corrosion potential after one hour of immersion in 3.55% NaCl that is higher in the positive direction than the corrosion potential of steel under the same conditions. Similar results have been reported for PAN coated metals like iron, steel, and stainless steel in salt water⁷.

The EIS data for all 29 coated and 1 uncoated panels were plotted in the Bode format. A qualitative comparison of all plots revealed that the coated panels have a higher impedance than the uncoated panel. Figure 1 shows the Bode plot of one of the coatings in comparison with the Bode plot obtained for an uncoated panel. Furthermore, the impedance spectra of all panels can be classified into two groups (labeled as A and B in Table 1): 21 coatings exhibit the characteristic Bode plot of a barrier coating (group A). Figure 2 shows Bode plots for several coatings in group A. These spectra were analyzed to find the corresponding equivalent circuit. The best fit was obtained for a circuit composed of a resistor in series with a capacitor (Figure 3). Figure 4 shows the experimental as well as the fitted data using the aforementioned equivalent circuit. The resistance has a value of 413.67 ohms and the capacitance was determined to be 0.103 nF. After one hour of immersion, the coatings in group A behaved as purely capacitive dielectrics. This behavior is similar to what has been found for epoxy or polyester coated steel panels in 3.5% NaCl for up to 1000 hours of immersion.⁸ Bode plots for the remaining 8 coatings show an inflection point which indicates that two time constants are present (group B). This may be caused by an electrochemical process taking place which could be indicative of coating failure. These coatings have a lower impedance than those in group A. Figure 5 shows Bode plots for selected coatings in group B (a group A coating was included in the figure for comparison). Due to complexity of the spectra and time constraints, the analysis of these plots will be performed at a later time.

Table 1. Thickness, color, corrosion potential, and EIS group of conductive polymer coatings

Panel No.	Thickness mils	Color	E_{corr} Volts	EIS Group
1	1.0	Clear	-0.4570	A
2	3.0	Clear	0.0090	B
3	3.0	Clear	-0.2210	A
4	1.0	Amber	-0.3860	A
5	2.0	Gray	0.0030	A
6	3.0	Clear	0.0580	B
7	1.0	Green	-0.0600	A
8	1.0	Gray	-0.0010	A
9	1.0	Clear	-0.0990	A
10	2.0	Green	-0.0080	B
11	1.0	Clear	-0.2090	A
12	1.0	Clear	-0.0900	A
13	1.0	Gray	-0.0570	A
14	2.0	Blue	-0.4560	A
15	3.0	Blue	-0.3100	B
16	1.0	Amber	-0.6380	A
18	3.0	Amber	-0.1110	A
20	3.0	Amber	-0.1600	A
19	1.0	Amber	-0.1260	A
20	3.0	Black	0.0020	B
21	3.0	Clear	-0.3040	B
22	1.0	Gray	-0.1320	B
23	1.0	Clear	-0.4450	B
24	1.0	Black	0.0230	A
25	1.0	Gray	-0.1160	A
26	1.0	Black	-0.4790	A
27	1.2	Clear	-0.1730	A
28	3.0	Amber	-0.1440	A
29	1.0	Green	-0.1400	A
Steel			-0.5400	

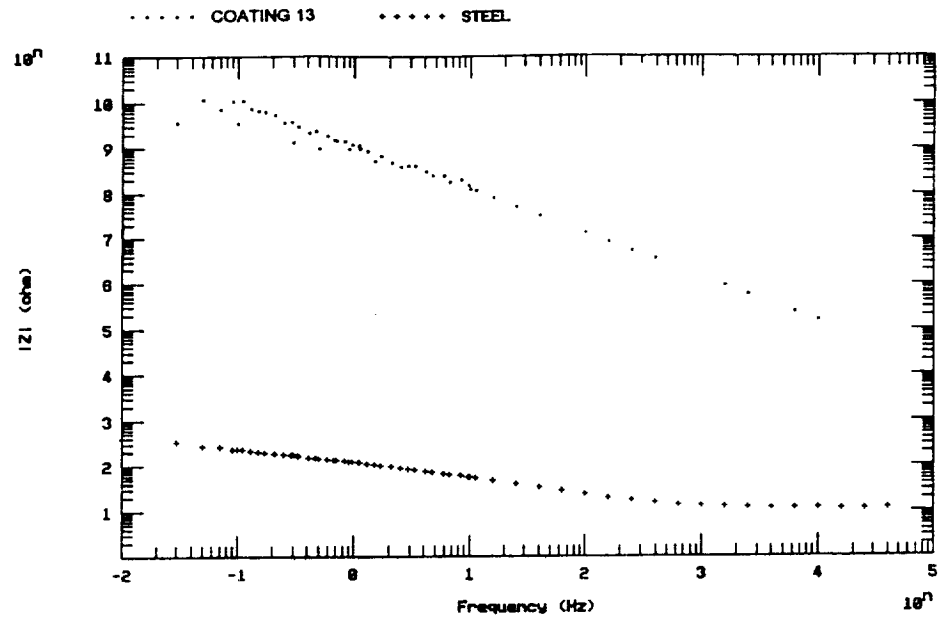


Figure 1. Bode plots for coating 13 and bare steel

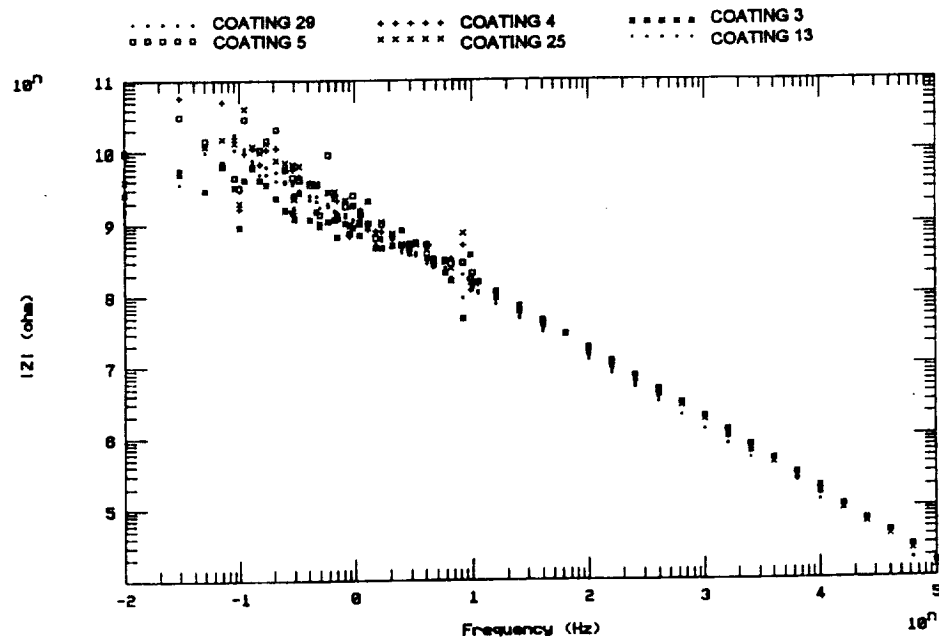


Figure 2. Bode plots for several coatings in group A

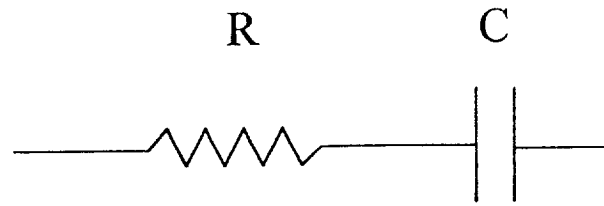


Figure 3. Equivalent circuit for Group A conductive polymer coatings

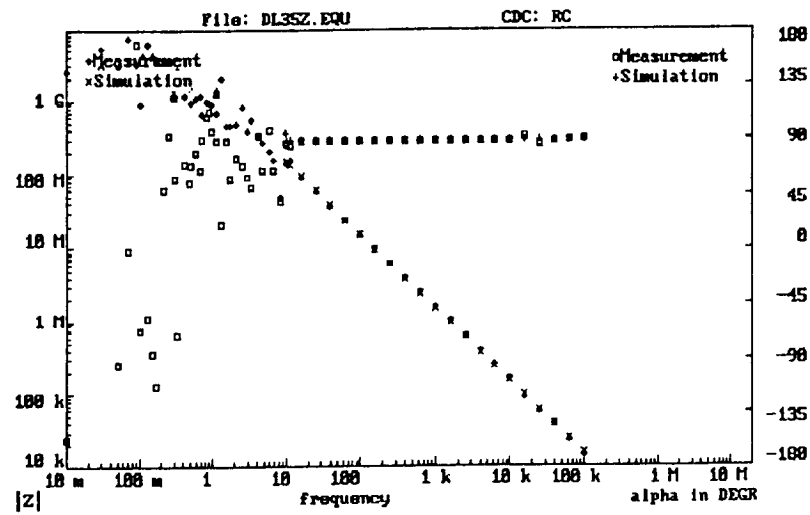


Figure 4. Experimental and simulated EIS data for conductive polymer coating 3

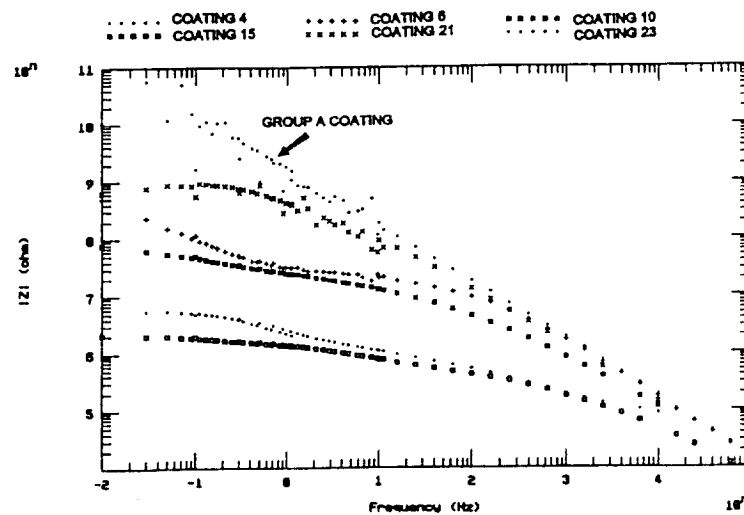


Figure 5. Bode plots for one coating in group A and several coatings in group B

4. CONCLUSION

Corrosion potential measurements of the twenty-nine coatings after one hour of immersion in 3.55% NaCl indicate that all but one of the coatings exhibit a corrosion potential that is shifted in the direction of noble metals.

EIS measurements showed that the coated panels have a higher impedance than bare steel. Qualitative observation of the Bode plots, allowed the classification of the coatings into two groups: coatings in group A exhibit an EIS spectra indicative of capacitive behavior; coatings in group B exhibit an EIS spectra with an inflection indicative of an electrochemical process. The experimental EIS data for coatings in group A can be simulated by using an equivalent circuit including a resistor in series with a capacitor. The EIS spectra of coatings in group B will be analyzed to find an equivalent circuit at a later date. Experiments using longer immersion times are currently underway.

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